JC09 Rec'd PCT/PTO 17 DEC 2001

FORM PTO-1390 (REV. 1-98) U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE **TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371**		ATTORNEY'S DOCKET NUMBER 41577/266144 U.S. APPLICATION NO. (If known, see 37 CFR 1.5) unknown 10/018727
INTERNATIONAL APPLICATION NO. PCT/GB00/02371	INTERNATIONAL FILING DATE 19 June 2000 (19.06.00)	PRIORITY DATE CLAIMED 18 June 1999 (18.06.99)
TITLE OF INVENTION FUNCTIONALISED SOLID SURFACES		
APPLICANT(S) FOR DO/EO/US WILLIS, Colin Robert; BADYAL, Jas Pal Singh; BREWER, Stuart Anson		

Applicants herewith submit to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a FIRST submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371.
3. ☐ This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 37 (b) and PCT Articles 22 and 39(1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as published (35 U.S.C. 371(c)(2))
   a. ☒ is transmitted herewith (required only if not transmitted by the International Bureau).
   b. ☐ has been transmitted by the International Bureau.
   c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☐ A translation of the published International Application into English (35 U.S.C. 371(c)(2)).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
   a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
   b. ☐ have been transmitted by the International Bureau.
   c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
   d. ☒ have not been made and will not be made.
8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371 (c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)). (unexecuted)
10. ☐ A translation of the annexes of the International Preliminary Examination Report under PCT Article 36
11. ☐ An Information Disclosure Statement under 37 CFR 1.197 and 1.98
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A FIRST preliminary amendment.
    ☐ A SECOND or SUBSEQUENT preliminary amendment.
14. ☐ A substitute specification.
15. ☐ A change of power of attorney and/or address letter.
16. ☒ Other items or information:
    a. Certification Under 37 CFR 1.10

    I hereby certify that this document is being mailed to Box PCT, Commissioner for Patents, P. O. Box 2327, Arlington, Virginia 22202, via "Express Mail Post Office to Addressee" on this 17th day of December, 2001, Express Mail Label No. EL209599984US

    Angela M. Rossi Angela M. Rossi

    b. Version with markings to show changes made
    c. International Preliminary Examination Report

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U.S. APPLICATION NO. (if known, see 37 CFR 1.5) 10/018727 unknown	INTERNATIONAL APPLICATION NO. PCT/GB00/02371	ATTORNEY'S DOCKET NUMBER 41577/266144

17. ☒ The following fees are submitted BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5)):		CALCULATIONS	PTO USE ONLY
Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2) paid to USPTO and International Search Report not prepared by the EPO or JPO	$1,040.00		
International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO	$890.00		
International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2) paid to USPTO	$740.00		
International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4)	$710.00		
International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4)	$100.00		
ENTER APPROPRIATE BASIC FEE AMOUNT	=	$890.00	
Surcharge of $130.00 for furnishing the oath or declaration later than ☐ 20 ☒ 30 months from the earliest claimed priority date (37 CFR 1.492(e)).		$.00	

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	$	
Total claims	20	00	X $18.00	$.00	
Independent claims	03	00	X $84.00	$.00	
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ $280.00	$.00	
TOTAL OF ABOVE CALCULATIONS			=	$890.00	
Reduction of ½ for filing by small entity, if applicable.			--	$.00	
SUBTOTAL			=	$890.00	
Processing fee of $130.00 for furnishing the English translation later than ☐20 ☐30 months from the earliest claimed priority date (37 CFR 1.492(f)).				$.00	
TOTAL NATIONAL FEE			=	$890.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). $40 per property				$.00	
TOTAL FEES ENCLOSED			=	$890.00	
				Amount to be refunded:	$
				charged:	$

a. ☒ Check in the amount of $890.00 is enclosed.

b. ☐ Please charge my Deposit Account No. 11-0855 in the amount of $______ to cover the above fees. A duplicate copy of this sheet is enclosed.

c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 11-0855.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b) must be filed and granted to restore the application to pending status.

Customer No. 23370

SEND ALL CORRESPONDENCE TO:

John S. Pratt, Esq.
KILPATRICK STOCKTON LLP
1100 Peachtree Street, Suite 2800
Atlanta, Georgia 30309-4530

Kristin Mallatt
SIGNATURE

Name: Kristin D. Mallatt
Registration No. 46,895

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10/018727
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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant:	Willis, et al.		
International Application No.:	PCT/GB00/02371		
International Filing Date:	19 June 2000 (19.06.00)		
Serial No.:		Group Art Unit:	
Filing Date:	17 December 2001	Examiner:	
For:	FUNCTIONALISED SOLID SURFACES		

Attorney Docket: 41577/266144
Date: 17 December 2001

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Commissioner for Patents
P. O. Box 2327
Arlington, Virginia 22202

PRELIMINARY AMENDMENT

Preliminary to any examination on the merits, Applicants respectfully submit the following amendments:

<u>In the Claims:</u>

Kindly rewrite the claims.as follows:

5. (Amended) A method according to claim 1, wherein the plasma discharge is pulsed.

6. (Amended) A method according to claim 2 wherein the plasma discharge is pulsed and the average power of the pulsed plasma discharge is less than $0.05W/cm^3$.

7. (Amended) A method according to claim 5, wherein the pulsed plasma discharge is applied such that power is on for 20μs and off for from 10000μs to 20000μs.

8. (Amended) A substrate having an epoxy containing coating thereon, obtained by a process according to claim 1.

9. (Amended) A method according to claim 1 which further comprises derivatization of the epoxy groups, suitably with a nucleophilic group.

12. (Amended) A method for immobilisation of a nucleophilic reagent at a surface, said method comprising the application of a reactive epoxy containing coating to said surface by a method according to claim 1, and then contacting the surface with a solution of said nucleophilic agent under conditions such that the nucleophilic agent reacts with the epoxy groups.

14. (Amended) A method according to claim 13, wherein the applying of the reactive coating to at least one of the said surfaces is performed using a method according to claim 1.

15. (Amended) A method according to claim 13 comprising the applying of a reactive coating to both said surfaces by plasma deposition, introducing a coupling agent between said surfaces, and allowing said coupling agent to react with reactive groups on each surface.

17. (Amended) A method according to claim 15 wherein said coupling agent is a diamine.

18. (Amended) A method according to claim 13 wherein said other surface includes nucleophilic groups able to react with said reactive groups so as to bring about adhesion.

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Version with markings to show changes made:

In the Claims:

Kindly amend the claims as follows:

5. (Amended) A method according to [any one of the preceding claims] claim 1, wherein the plasma discharge is pulsed.

6. (Amended) A method according to claim 2 wherein the plasma discharge is pulsed and the average power of the pulsed plasma discharge is less than 0.05W/cm^3.

7. (Amended) A method according to [any one of the preceding claims] claim 5, wherein the pulsed plasma discharge is applied such that power is on for 20μs and off for from 10000μs to 20000μs.

8. (Amended) A substrate having an epoxy containing coating thereon, obtained by a process according to [any one of the preceding claims] claim 1.

9. (Amended) A method according to [any one of] claim[s] 1 [to 7] which further comprises [the step of] derivatization of the epoxy groups, suitably with a nucleophilic group.

12. (Amended) A method for immobilisation of a nucleophilic reagent at a surface, said method comprising the application of a reactive epoxy containing coating to said surface by a method according to [any one of] claim[s] 1 [to 7], and then contacting the surface with a solution of said nucleophilic agent under conditions such that the nucleophilic agent reacts with the epoxy groups.

14. (Amended) A method according to claim 13, wherein the applying of the reactive coating to at least one of the said surfaces is performed using a method according to [any one of] claim[s] 1 [to 7].

15. (Amended) A method according to [either of] claim[s] 13 [or 14] comprising the applying of a reactive coating to both said surfaces by plasma deposition, introducing a coupling agent between said surfaces, and allowing said coupling agent to react with reactive groups on each surface.

17. (Amended) A method according to [either of] claim[s] 15 [or 16] wherein said coupling agent is a diamine.

18. (Amended) A method according to [either of] claim[s] 13 [or 14] wherein said other surface includes nucleophilic groups able to react with said reactive groups so as to bring about adhesion.

Remarks

Applicants submit that none of the above amendments are being made for reasons related to patentability, but are instead being made to put the application in proper format. Applicants believe no new matter has been added.

Respectfully submitted,

Kristin Mallatt

Kristin D. Mallatt
Reg. No. 46,895

OF COUNSEL:

KILPATRICK STOCKTON LLP
1100 Peachtree Street
Suite 2800
Atlanta, GA 30309-4530
404.815.6147
Attorney Docket No.: 47192/261776

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10/018727

IN THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US)

Applicants:	WILLIS, Colin Robert, BADYAL, Jas Pal Singh, And BREWER, Stuart Anson
International Application No.:	PCT/GB00/02371
U.S. Serial No.:	10/018,727
International Filing Date:	19 June 2000 (19.06.00)
U.S. Filing Date:	05 December 2001 (05.12.01)
For:	FUNCTIONALISED SOLID SURFACES

Box PCT
Commissioner for Patents
Washington, D.C. 20231

Attorney Docket No. 41577/266144
Date: 17 April 2002

SECOND PRELIMINARY AMENDMENT

Sir:

Kindly amend the above-identified patent application prior to examination:

On page 1, immediately following the title "Functionalised Solid Surfaces" kindly insert the following paragraph:

--This application claims priority to Great Britain Patent Application No. 9914185.5 filed on June 18, 1999; Great Britain Patent Application No. 0001514.9 filed on January 25, 2000; and International Application No. PCT/GB00/02371 filed on June 19, 2000 and published in English as International Publication No. WO 00/78469 A2 on December 28, 2000.--

Respectfully submitted,

Kristin Mallatt

Kristin D. Mallatt
Reg. No. 46,895

KILPATRICK STOCKTON LLP
1100 Peachtree Street, Suite 2800
Atlanta, Georgia 30309
(404) 815-6147

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Functionalised Solid Surfaces

The present invention relates to the production of coatings which contain epoxy functional groups, using pulsed plasma polymerisation of compounds such as glycidyl methacrylate. Such surfaces can be subject to subsequent derivatisation with other functional groups, such as nucleophilic reagents, or they may be used to promote adhesion and as adhesives.

The surface functionalisation of solid objects is a topic of considerable technological importance, since it offers a cost-effective means for improving substrate performance without affecting the overall bulk properties. For instance, epoxy groups at a surface can provide binding sites for the immobilisation of nucleophilic reagents (Rosowsky, A. In *Heterocyclic Compounds with Three- and Four- Membered Rings*, Weissberger, A. Ed.; The Chemistry of Heterocyclic Compounds; Interscience Publishers: New York, 1964; Part 1), such as amines (Zhang, J. et al., *J. Polym. Sci., Part A: Polym. Chem.*, **1995**, 33, 2629; Mori, M. et al., *J. Polym. Sci., Part A:* Polym. Chem., **1994**, 32, 1683; Allmer, K. et al., *J. Polym. Sci., Part A:* Polym. Chem., **1989**, 27, 1641; Allcock, H. R. et al., *Chem. Mater.*, **1994**, 6, 516; Lee, W. et al., *J. Colloid Interface Sci.*, **1998**, 200, 66; Kubota, H. et al., *J. Appl. Polym. Sci.*, **1995**, 56, 25). These reactions find application in biotechnology (Lee, W.; Furusaki, et al., *J. Colloid Interface Sci.*, **1998**, 200, 66; Kubota, H. et al., *J. Appl. Polym. Sci.*, **1995**, 56, 25; Bai, G. et al., *Polym. Bull.*, **1996**, 36, 503; Motomura, T. et al., Eur. Pat. Appl. 679436, 1999) and adhesion (Zhang, J. et al., *J. Polym. Sci., Part A: Polym. Chem.*, **1995**, 33, 2629; Shang, M. C. et al., *Polymer*, **1999**, 40, 299; Wu, S. et al., *Macromolecules*, **1999**, 32, 186; Yamada, K. et al., *J. Appl. Polym. Sci.*, **1996**, 60, 1847; Wang, T. et al., *J. Adhes. Sci. Tech.*, **1997**, 11, 679). Existing methods of attaching epoxides onto solid surfaces include UV (Allmer, K. et al., *Polym. Sci., Part A:* Polym. Chem., **1989**, 27, 1641; Allcock, H.

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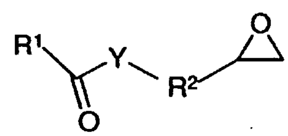
R. et al., *Chem. Mater.*, **1994**, 6, 516; Bai, G. et al., *Polym. Bull.*, **1996**, 36, 503; Wu, S. et al., *Macromolecules*, **1999**, 32, 186) or electron beam (Lee, W. et al., *J. Colloid Interface Sci.*, **1998**, 200, 66) irradiation of substrates immersed in a solution containing an initiator and a polymerisable epoxy monomer (e.g. glycidyl methacrylate) leading to polymer growth at the surface. Other possibilites encompass plasma activation of a substrate followed by solution phase grafting of a polymerisable epoxy monomer (Mori, M. et al., *J. Polym. Sci., Part A:* Polym. Chem., **1994**, 32, 1683; Yamada, K. et al., *J. Appl. Polym. Sci.*, **1996**, 60, 1847), or coupling epoxysilanes onto silicon wafers (Luzinov, I. et al., *Langmuir*, **1999**, 15, 3029). All of these approaches suffer from drawbacks such as involving multistep processes and the requirement for solution phase chemistry. Some may also show a tendency to be substrate-specific.

Plasma polymers are often regarded as being structurally dissimilar compared to conventional polymers, since they possess high levels of cross-linking and lack a regular repeat unit (Yasuda, H. *Plasma Polymerisation* Academic Press: New York, 1985). This can be attributed to the plasma environment generating a whole range of reactive intermediates which contribute to the overall lack of chemical selectivity. However, it has been found that pulsing the electric discharge on the ms-μs timescale can significantly improve structural retention of the parent monomer species (Panchalingam, V. et al., *Appl. Polym. Sci.* **1994**, 54, 123; Han, L. M. et al., *Chem. Mater.*, **1998**, 10, 1422; Timmons et al., US patent no. US 5,876,753) and in some cases conventional linear polymers have been synthesised (Han, L. M. et al., *J. Polym. Sci., Part A: Polym. Chem.* **1998**, 36, 3121). Under such conditions, repetitive short bursts of plasma are understood to control the number and lifetime of active species created during the on-period, which then is followed by conventional reaction

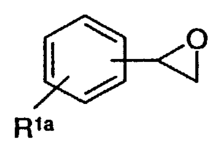
pathways occurring during the off-period (e.g. polymerisation) (Savage, C. R. et al.,*Chem. Mater.*, **1991**, 3, 575).

The applicants have found that plasma polymerisation of monomers containing epoxy functionalities can potentially overcome the limitations of existing techniques for forming epoxy functionalised surfaces.

According to the present invention there is provided a method for applying a reactive epoxy containing coating to a substrate, said method comprising subjecting said substrate to a plasma discharge in the presence of a compound of formula (I) or (IA)



(I)



(IA)

where R^1 or R^{1a} is an optionally substituted hydrocarbyl group or heterocyclic group;
R^2 is an optionally substituted straight or branched alkylene chain; and
Y is oxygen or a bond.

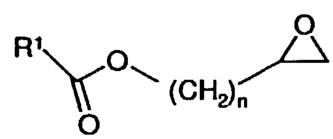
As used herein, the term "hydrocarbyl" includes alkyl, alkenyl, alkynyl, aryl and aralkyl groups. The term "aryl" refers to aromatic cyclic groups such as phenyl or naphthyl, in particular phenyl. The term "alkyl" refers to straight or branched chains of carbon atoms, suitably of from 1 to 20

carbon atoms in length. The terms "alkenyl" and "alkynyl" refer to straight or branched unsaturated chains suitably having from 2 to 20 carbon atoms. These groups may have one or more multiple bonds. Thus examples of alkenyl groups include allenyl and dienyl.

Suitable optional substituents for hydrocarbyl groups R^1 and R^{1a} and alkylene groups R^2 are groups that are substantially inert during the process of the invention. They may include halo groups such as fluoro, chloro, bromo and iodo. Particularly preferred halo substituents are fluoro.

Preferably Y is oxygen.

In particular, R^2 is an unsubstituted alkylene group. Thus, in a particular embodiment, the compound of formula (I) is a compound of formula (II)



(II)

where R^1 is as defined above and n is an integer of from 1 to 20, for example from 1 to 3 and preferably 1.

Suitably R^1 and R^{1a} are unsaturated hydrocarbyl groups such as alkenyl or alkynyl. In particular, R^1 or R^{1a} is a C_{1-6} straight or branched alkenyl group. These may be optionally substituted as defined above.

A particularly preferred compound of formula (II) are acrylates of formula (III)

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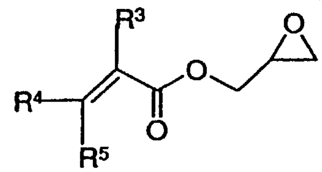
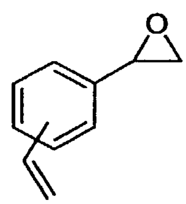


(III)

where R^3, R^4 and R^5 are independently selected from hydrogen or alkyl, and in particular, from hydrogen or C_{1-6} alkyl, such as methyl.

A particular example of a compound of formula (III) is glycidyl methacrylate where R^3 is methyl, and R^4 and R^5 are both hydrogen.

A particular example of a compound of formula (IA) is a divinylbenzene monoxide of formula (IV)



(IV)

Precise conditions under which the plasma deposition of the compound of formula (I) or (IA) takes place in an effective manner will vary depending upon factors such as the nature of the monomer, the substrate etc. and will be determined using routine methods and/or the techniques illustrated hereinafter. In general however, polymerisation is suitably effected using vapours of compounds of formula (I) or (IA) at pressures of from 0.01 to 10 mbar, suitably at about 0.2mbar.

A glow discharge is then ignited by applying a high frequency voltage, for example at 13.56MHz.

The applied fields are suitably of average power of up to 50W.

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Suitable conditions include pulsed or continuous fields, but are preferably pulsed fields.

The fields are suitably applied for a period sufficient to give the desired coating. In general, this will be from 30 seconds to 20 minutes, preferably from 2 to 15 minutes, depending upon the nature of the compound of formula (I) or (IA) and the substrate etc.

Suitably, the average power of the pulsed plasma discharge is low, for example of less than $0.05W/cm^3$, preferably less than $0.025W/cm^3$ and most preferably less than $0.0025W/cm^3$.

The pulsing regime which will deliver such low average power discharges will vary depending upon the nature of the substrate, the size and nature of the discharge chamber etc. However, suitable pulsing arrangements can be determined by routine methods in any particular case. A typical sequence is one in which the power is on for 20μs and off for from 10000μs to 20000μs.

Suitable plasmas for use in the method of the invention include non-equilibrium plasmas such as those generated by radiofrequencies (Rf), microwaves or direct current (DC). They may operate at atmospheric or sub-atmospheric pressures as are known in the art.

The plasma may comprise the monomeric compound alone, in the absence of other gases or in mixture with for example an inert gas. Plasmas consisting of monomeric compound alone may be achieved as illustrated hereinafter, by first evacuating the reactor vessel as far as possible, and then purging the reactor vessel with the organic compound for a period sufficient to ensure that the vessel is substantially free of other gases. The temperature in the plasma chamber is suitably high enough to allow sufficient monomer in gaseous phase to enter the plasma chamber. This will depend upon the monomer and

conveniently ambient temperature will be employed. However, elevated temperatures for example from 25 to 50°C may be required in some cases.

The invention further provides a substrate having an epoxy containing coating thereon, obtained by a process as described above. Such substrates will include any solid substrate, such as fabric, metal, glass, ceramics, paper, wood or polymers such as polytetrafluoroethylene, polythene or polystyrene. In a particular embodiment, the surface comprises a support material such as a polymeric material used in biochemical analysis.

When the invention is used in the field of adhesives, the substrate may be any of the above-listed substrates, but is likely to be glass, ceramic, metal, paper, wood or polymer.

The pulsed plasma polymerisation of the invention is therefore a solventless method for functionalising solid surface with epoxy groups.

Once the epoxy functional coating has been applied to the substrate, the epoxy group may be further derivatised as required. In particular, it may be reacted with a carboxylic acid such as trifluoroacetic acid, an amine such as diethylamine or an amino acid. The derivatisation reaction may be effected in the gaseous phase where the reagents allow, or in a solvent such as an organic solvent. Examples of such solvents include alcohols such as methanol, and tetrahydrofuran.

The derivatisation may result in the immobilisation of a nucleophilic reagent on said surface.

Epoxide functionalised surfaces produced in accordance with the invention were derivatized with a variety of nucleophilic reagents (e.g. carboxylic acids and amines). Typically, reaction occured at the electrophilic epoxide carbon centres leading to ring opening. In the case of carboxylic acids and amines, attack on the less substituted epoxide carbon is favoured giving rise to the secondary alcohol, Scheme I.

Thus in a further embodiment, the invention provides a method for immobilisation of a nucleophilic reagent at a surface, said method comprising the application of a reactive epoxy containing coating to said surface by a method described above, and then contacting the surface with a solution of said nucleophilic agent under conditions such that the nucleophilic agent reacts with the epoxy groups.

Curing of the epoxy groups in the coating may result in the adhesion of the surface to another surface. Thus in yet a further aspect, the invention provides a method for adhering two surfaces together, said method comprising applying a reactive coating to at least one of said surfaces by plasma deposition, and contacting said surface with the other surface under conditions whereby reactive groups in the coating will react so as to secure the two surfaces together. It is preferred that the reactive coating is applied to at least one of the surfaces using a method as described herein.

Suitably the other surface itself contains reactive functionalities, in particular nucleophilic groups such as amine or acid groups which will react with the reactive groups in the coating so as to join the surfaces together. The reactive groups are preferably epoxide groups. Where such nucleophilic groups are not used, coupling agents may be employed.

In a particular embodiment, a reactive epoxy containing coating is applied to both said surfaces using a method as described

above, a coupling agent such as a diamine, for example, ethylene diamine, is introduced therebetween. The coupling agent is then allowed to react with epoxy groups on each surface, resulting in adhesion between the surfaces.

If necessary or desired, adhesion may be enhanced by first roughening the surface. This may be achieved by O_2 plasma roughening (M. Morra et al., Surf. Interf. Anal. 1990, 16, 412; Ryan et al., Macromolecules 1995, 28, 1377).

Pulsed plasma polymerization in accordance with the invention has been found to be an effective means for functionalizing solid substrates with epoxide groups. The resulting functionalised surfaces are amenable to conventional epoxide derivatization chemistries. In addition they have been found to offer excellent adhesion performance.

The invention will now be particularly described by way of example with reference to the accompanying diagrammatic drawings and reaction schemes in which:

Figure 1 shows the C(1s) XPS spectra of glycidyl methacrylate plasma polymers deposited onto a flat glass substrate: (a) theoretical curve; (b) 3 W continuous wave; and (c) pulsed (time on = 20 μs, time off = 20 ms, peak power = 40 W).

Figure 2 shows the infrared spectra of: (a) glycidyl methacrylate monomer; (b) 3 W continuous wave plasma polymer; and (c) pulsed plasma polymer (time on = 20 μs, time off = 20 ms, peak power = 40 W).

Figure 3 shows the C(1s) XPS spectra of plasma polymers exposed to trifluoroacetic acid vapour: (a) 3 W continuous wave; and (b) pulsed (time on = 20 μs, time off = 20 ms, peak power = 40 W).

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Figure 4 shows the N(1s) and C(1s) XPS spectra of glycidyl methacrylate pulsed plasma polymer derivatised with diethyleeamine (time on = 20 μs, time off = 20 ms, peak power = 40 W).

Figure 5 shows stress/strain curves of: (a) polyethylene substrate, and (b) single lap joint of pulsed glycidyl methacrylate plasma polymer coated polyethylene strips (time on = 20 μs, time off = 20 ms, peak power = 40 W).

Figure 6 shows the influence of 20 W oxygen plasma pretreatment time upon lap joint strength for PTFE substrate which were subsequently coated with pulsed glycidyl methacrylate plasma polymer (time on = 20 μs, time off = 20 ms, peak power = 40 W).

Figure 7 shows the C(1s) XPS spectra of 3W continuous wave allyl glycidyl ether plasma polymer.

Figure 8 shows the infrared spectra of: (a) allyl glycidyl ether monomer; (b) 3 W continuous wave plasma polymer; and (c) pulsed plasma polymer (time on = 20 μs, time off = 20 ms, peak power = 40 W).

Figure 9 shows the infrared spectra of: (a) butadiene monoxide monomer; (b) 3 W continuous wave plasma polymer; and (c) pulsed plasma polymer (time on = 20 μs, time off = 20 ms, peak power = 40 W).

Scheme 1 illustrates the reaction between an epoxide ring and a nucleophilic reagent, where R is an organic residue and R^1 is a nucleophilic group.

Scheme 2 illustrates the reaction of poly(glycidyl methacrylate) with trifluoroacetic acid.

Scheme 3 illustrates the reaction of poly(glycidyl methacrylate) with diethylamine.

Example 1

Plasma polymerization of glycidyl methacrylate (Aldrich, +97%, further purified using several freeze-pump-thaw cycles) was carried out in a cylindrical glass reactor pumped by a mechanical rotary pump via a liquid nitrogen cold trap (base pressure = 8×10^{-3} torr, and leak rate = 3.2×10^{-9} mol s^{-1}). A copper coil wrapped around the reactor was coupled to a 13.56 MHz radio frequency power supply via an LC matching network. Prior to each experiment, the chamber was cleaned using a 50 W air plasma at 0.2 torr. Glycidyl methacrylate monomer was then introduced via a fine control needle valve at a pressure of 0.2 torr and 1.2×10^{-7} mol s^{-1} flow rate, followed by film deposition for 15 mins. The reactor was purged with monomer vapour for 5 minutes following plasma deposition. In the case of pulsed plasma polymerization, a signal generator was used to trigger the RF supply, and the pulse shape was monitored with an oscilloscope.
Quartz crystal deposition rate measurements were carried out during plasma polymerization using a Varian 985-7013 thickness monitor.

XPS analysis of the glycidyl methacrylate plasma polymer coatings obtained confirmed the presence of only carbon and oxygen at the surface, with no Si(2p) signal from the underlying glass substrate showing through. The C(1s) envelope contained a variety of carbon functionalities for both the continuous wave and pulsed plasma polymer layers: $\underline{C}H$ (285.0 eV), $\underline{C}(CH_3)(C{=}O)O$ (285.7 eV), $O\text{-}\underline{C}H_2\text{-}CO$ (286.7 eV), epoxide carbons (287.2 eV), $\underline{C}{=}O$ (287.8 eV), and $\underline{C}({=}O)O$ (289.1 eV), Figure 1. Apart from the carbonyl group at 287.8 eV (associated with the continuous wave plasma polymer), the remaining peak assignments are referenced to XPS spectra obtained from conventional solution phase polymerised glycidyl methacrylate. Pulsed plasma polymerization produced a much larger

concentration of epoxide groups compared to continuous wave conditions, Figure 1 and Table 1.

Table 1: XPS analysis of glycidyl methacrylate plasma polymers.

Conditions	C(1s)		Atomic %	
	% Epoxy	% (C=O)O	% C	% O
Continuous wave	7.1±0.5	6.5±0.5	77.5±0.5	22.5±0.5
Pulsed	19.1±0.5	10.6±0.3	73±1	27±1
Theoretical	20.0	10.0	70.0	30.0

Infrared spectra of plasma polymer films deposited onto NaCl plates were acquired on a Mattson Polaris FTIR instrument at a resolution of 4 cm^{-1} and averaged over 100 scans.

Infrared spectroscopy was used to probe the molecular structure of the plasma deposited coatings, Figure 2. For the glycidyl methacrylate monomer, the following band assignments were made: epoxide ring C-H stretching (3063 cm^{-1}), C-H stretching (3000-2900 cm^{-1}), acrylate carbonyl stretching (1720 cm^{-1}), acrylate C=C stretching (1637 cm^{-1}), epoxide ring breathing (1253 cm^{-1}), antisymmetric epoxide ring deformation (908 cm^{-1}), and symmetric epoxide ring deformation (842 cm^{-1}). The weak absorption feature present at 2360 cm^{-1} originates from background CO_2 present in the FTIR spectrometer. Continuous wave plasma deposition of glycidyl methacrylate gave rise to broad infrared absorption features: epoxide ring C-H stretching (3060 cm^{-1}), C-H stretching (3000-2900 cm^{-1}), saturated ester C=O stretching (1728 cm^{-1}), C=C stretching (1630 cm^{-1}), epoxide ring breathing (1253 cm^{-1}), antisymmetric epoxide ring deformation (908 cm^{-1}), and symmetric epoxide ring deformation (842 cm^{-1}). The epoxide ring and carbon-carbon double bond features were much weaker compared to the monomer, whereas the C-H stretching region was more intense. All the bands associated with the glycidyl methacrylate monomer were clearly discernible following pulsed plasma polymerization, except for the acrylate carbon-carbon

double bond feature which had disappeared during polymerization. The more intense infrared absorption bands belonging to the epoxide ring confirmed that greater structural retention had occurred during electrical pulsing conditions.

Quartz crystal deposition rate measurements provided values of $19 \pm 3 \times 10^{-9}$ g s^{-1} cm^{-2} and $2.5 \pm 0.5 \times 10^{-9}$ g s^{-1} cm^{-2} for the continuous wave and the pulsed conditions respectively. The lower value obtained for pulsed plasma polymerization can be mainly attributed to less energy input. In fact the deposition efficiency (expressed as deposition rate divided by power) was calculated to be 6.3 and 63×10^{-9} g cm^{-2} J^{-1} respectively.

Example 2

The epoxide functionalized surfaces were then reacted with trifluoroacetic acid vapour (Fluorochem Limited, +99.5%) for 30 min followed by evacuation in order to remove any absorbed remnants. Other derivatization reactions included exposure to ethylenediamine (Aldrich, +99%), and diethylamine (Sigma, +98%); here plasma polymer coated glass slides were immersed into a solution of the amine diluted with methanol (Fisher, +99.8%) for 24 hrs, and then rinsed in pure methanol.
X-ray photoelectron spectroscopy (XPS) analysis was performed using a Kratos ES300 spectrometer equipped with a Mg Kα X-ray source and an hemispherical analyser operating in fixed retard ratio mode (22:1). Photoelectrons were collected at a take off angle of 30° from the substrate normal. The elemental composition was calculated using sensitivity factors derived from chemical standards, C : O : F : N equals 1.00 : 0.57 : 0.67 : 0.74. All binding energies were referenced to the C(1s) hydrocarbon peak at 285.0 eV. A Marquardt minimization computer program was used to fit core level envelopes with fixed width Gaussian peaks.

Trifluoroacetic acid vapour underwent reaction to a greater extent with the pulsed plasma polymer coating (XPS measured 4.1

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± 0.5% and 16.0 ± 0.8% fluorine for the continuous and pulsed plasma polymer coatings respectively), Scheme 2. This enhancement for the pulsed plasma polymer coating was confirmed by the identification of $\underline{C}F_3$ functionalities at 293.4 eV in the C(1s) envelope, Figure 3. The proportion of epoxide groups which had undergone monoesterification was calculated using the F(1s) peak area as follows:

$$\%[F] = \frac{\frac{3}{2}x[Epoxide]_0}{[C]_0 + [O]_0 + \frac{7}{2}x[Epoxide]_0} \text{ x } 100 \qquad (1)$$

where x is the fraction of reacted epoxides, $[Epoxide]_0$ is the initial concentration of epoxide groups, $[C]_0$ is the initial concentration of carbon, $[O]_0$ is the initial concentration of oxygen, and $[F]$ is the percentage of fluorine detected at the surface. On this basis, 42% and 89% of the surface epoxide groups had reacted for the continuous wave and pulsed plasma polymer layers respectively. Therefore it appears that the proportion of epoxide group centres calculated from the C(1s) peak fitting (Figure 1) is probably an overestimation for continuous wave conditions. Other groups such as ethers or carbonyls must also be present in the plasma polymer layer contributing to the component at around 287.2 eV in the C(1s) spectrum. Excess trifluoroacetic acid could potentially react further with alcohol groups formed during epoxide ring opening to produce a diester and this may contribute to a slight overestimation in the overall reaction yield.

Diethylamine was used to assess the reactivity of surface epoxide groups towards amines. This secondary amine was chosen because it is capable of reacting only once with an epoxide centre, Scheme 2; therefore making it much easier to calculate the number of aminated epoxides from the corresponding N(1s) peak area:

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$$\%[N] = \frac{\frac{1}{2}x[Epoxide]_0}{[C]_0 + [O]_0 + \frac{5}{2}x[Epoxide]_0} \times 100 \tag{2}$$

4.4% nitrogen was detected by XPS for the pulsed plasma polymer layer, which corresponds to 59% of the surface epoxide groups having undergone reaction as depicted in Scheme 2. The two peaks seen in the N(1s) spectra can be assigned to neutral (399.8 eV) and positively charged nitrogen (402.1 eV), Figure 4, where the latter is probably due to protonation by atmospheric moisture, rather than the reaction of the amine centre with an adjacent epoxide group.

Example 3

For the adhesion measurements, a drop (~ 3 µl) of a coupling agent solution (ethylenediamine 0.5 M in 1,4-dioxane (Aldrich, +99%)) was placed between two glycidyl methacrylate plasma polymer coated strips of polymer film (polyethylene, PE, ICI, 0.08 mm thickness, or polytetrafluoroethylene, PTFE, Goodfellow, 0.25 mm thickness) and then cured overnight at 60°C. Subsequently, single lap adhesion tests were carried out using an Instron 5543 tensilometer operating at a crosshead speed of 1 mm min^{-1}.

The results of the single lap adhesion test measurements showed that the adhesive bond was stronger than the threshold for failure of the host polyethylene matrix (bulk failure occurred at 17 N), Figure 5. No adhesion between polyethylene strips was observed in the absence of either the epoxide functionalities or the curing agent.

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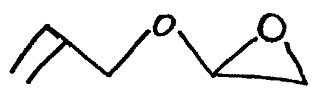
In the case of PTFE, O_2 plasma roughening of the substrate was needed prior to pulsed plasma deposition of glycidyl methacrylate in order to achieve good adhesion. Here the joint eventually failed rather than the substrate, since PTFE was much stronger than PE (bulk failure of PTFE occurred at 45 N). The duration of oxygen plasma pretreatment was found to affect the strength of the adhesive joint, Figure 6. Excessively long oxygen plasma exposures could be leading to polymer chain scission and the formation of low molecular weight material, which will have a detrimental effect upon adhesion.

<u>Example 4</u>

The methodology of example 1 was used in attempts to deposit films of allyl glycidyl ether (structure V).



(V)

This material was cited in US 5,876,753 as being suitable for use in plasma deposition to generate polymeric films. Films were produced using 3W continuous wave and pulsed plasma techniques. The films were subsequently analysed using XPS and IR spectroscopy.

Results of XPS analysis are summarised in Table 2. This shows that none of the deposited films show molecular structures that one would expect from the polymerised monomer when it undergoes conventional polymerisation via the C=C bond. The theoretical values were calculated from the conventional molecular structure of the polymerised allyl glycidyl ether.

Film	%C	%O	%Si
Theoretical	75	25	0
A - Continuous wave (3W, 30mins.)	86	14	0
B - Pulsed 30min	49	35	16
C - Pulsed 90min	61	30	9
Glass slide	23	53	24

Table 2 - elemental analysis of allyl glycidyl ether coatings as determined by XPS

Typical errors of ±2% on measured values.

Note that the key parameters for the pulsed deposition are time on=20μs, time off=20ms, peak power=40W.

The characterisation of each film will now be discussed in more detail.

<u>Film A - deposited by 3W continuous wave method</u>

The film deposited by the continuous wave method showed a depletion in oxygen content with respect to the theoretical value. No Si(2p) peak was observed from the glass substrate, indicating that a film of reasonable thickness was produced. The C(1s) XPS spectrum of the film is shown in Figure 7. The spectra are characterised by a strong hydrocarbon peak (285.0eV), but other functionalities are discernible such as C-O (286.5eV) and C=O (288.2eV). The latter functionality is not present in the monomer and could be due to rearrangement of the molecule in the plasma environment. The IR spectrum (Figure 8) indicates the presence of C=O groups ($1728cm^{-1}$), whilst a small amount of epoxy functionality is retained, indicated by the small peaks at $1259cm^{-1}$ and $848cm^{-1}$. The C=O peak overlaps with the C=C peak which has not disappeared.

These data indicate that continuous wave deposition causes films to be deposited in which most of the epoxy functionality

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has been removed. This is not desired to achieve the aims of the invention in suit.

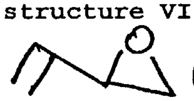
Films B and C - deposited by pulsed method

The pulsed plasma technique produced very slow deposition rates, evidenced by the presence of Si peaks in the XPS spectra of both films B and C. The C(1s) envelope showed a functionalised carbon with the presence of both C-O and C=O moieties. This indicates that some of the epoxy functionality has been lost. The IR spectra of films B and C were very poor (an example of which can be seen in Figure 8).

This work indicates that the method of the present invention shows unexpected advantages over the work of Timmons. The continuous wave and pulsed methods using the allyl gycidyl ether produce films in which a substantial amount of epoxy functionality has been lost. Furthermore, the deposition process using the pulsed technique is unacceptably slow. The method of the present invention suffers from neither of the problems suffered by an analogous method using allyl glycidyl ethers.

Example 5

The methodology of example 1 was used to try to deposit films of butadiene monoxide (structure VI).



(VI)

Results of XPS analysis are summarised in Table 3. This shows that none of the deposited films show molecular structures that one would expect from the polymerised monomer when the monomer undergoes conventional polymerisation. The theoretical values were calculated from the conventional molecular structure of the polymerised butadiene monoxide.

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Film	%C	%O	%Si
Theoretical	80	20	0
D - Continuous wave (3W, 30mins.)	89	11	0
E - Pulsed 30min	54	35	11
Glass slide	23	53	24

Table 3 - elemental analysis of butadiene monoxide coatings as determined by XPS

Typical errors of ±2% on measured values.

Note that the key parameters for the pulsed deposition are time on=20μs, time off=20ms, peak power=40W.

The characterisation of each film will now be discussed in more detail.

Film D - deposited by 3W continuous wave method

The film deposited by the continuous wave method showed a depletion in oxygen content with respect to the theoretical value. No Si(2p) peak was observed from the glass substrate, indicating that a film of reasonable thickness was produced. The IR spectrum (Figure 9) indicates the presence of C=O groups (ça 1730cm^{-1}). It is difficult to determine whether a small amount of epoxy functionality is retained; this would be indicated by the presence of peaks at ça 1259cm^{-1} and 848cm^{-1}.

These data indicate that continuous wave deposition causes films to be deposited in which most, if not all, of the epoxy functionality has been removed. This is not desirable, given the aims of the invention in suit.

Films E - deposited by pulsed method

The pulsed plasma technique produced very slow deposition rates, evidenced by the presence of Si peaks in the XPS spectra of film E. The IR spectrum of film E was very weak (see Figure

9). This is consistent with the existence of a very thin coating.

This work indicates that the method of the present invention shows unexpected advantages over the work of Timmons. The continuous wave method using the butadiene monoxide produces films in which a substantial amount of epoxy functionality has been lost. Furthermore, the deposition process using the pulsed technique is unacceptably slow. The method of the present invention suffers from neither of the problems suffered by an analogous method using butadiene monoxide.

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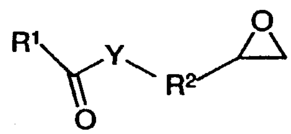
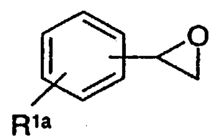
Claims

1. A method for applying a reactive epoxy containing coating to a substrate, said method comprising subjecting said substrate to a plasma discharge in the presence of a compound of formula (I) or (IA)



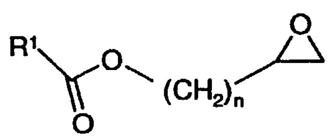
(I)



(IA)

where R^1 or R^{1a} is an optionally substituted hydrocarbyl group or heterocyclic group;
R^2 is an optionally substituted straight or branched alkylene chain; and
Y is oxygen or a bond.

2. A method according to claim 1 wherein the epoxy containing organic compound is a compound of formula (II)

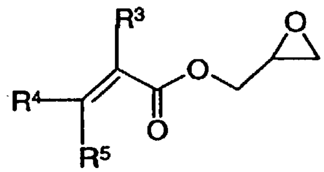


(II)

where R^1 is as defined in claim 1 and n is an integer of from 1 to 20.

3. A method according to claim 2 wherein, in the compound of formula (II), n is 1 to 3.

4. A method according to claim 3 wherein the compound of formula (II) is a compound of formula (III)



(III)

where R^3, R^4 and R^5 are independently selected from hydrogen or C_{1-6}alkyl.

5. A method according to any one of the preceding claims wherein the plasma discharge is pulsed.

6. A method according to claim 2 wherein the average power of the pulsed plasma discharge is less than $0.05 W/cm^3$.

7. A method according to any one of the preceding claims wherein the pulsed plasma discharge is applied such that power is on for 20μs and off for from 10000μs to 20000μs.

8. A substrate having an epoxy containing coating thereon, obtained by a process according to any one of the preceding claims.

9. A method according to any one of claims 1 to 7 which further comprises the step of derivatization of the epoxy groups, suitably with a nucleophilic group.

10. A method according to claim 9 wherein said further derivatization is by reaction with a carboxylic acid or an amine.

11. A method according to claim 10 wherein a solution of said carboxylic acid or amine is contacted with the surface under conditions in which the acid or amine functionality reacts with epoxy groups on the surface.

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12. A method for immobilisation of a nucleophilic reagent at a surface, said method comprising the application of a reactive epoxy containing coating to said surface by a method according to any one of claims 1 to 7, and then contacting the surface with a solution of said nucleophilic agent under conditions such that the nucleophilic agent reacts with the epoxy groups.

13. A method for adhering two surfaces together, said method comprising applying a reactive coating to at least one of said surfaces by plasma deposition, and contacting said surface with the other surface under conditions whereby reactive groups in the coating will react so as to secure the two surfaces together.

14. A method according to claim 13, wherein the applying of the reactive coating to at least one of the said surfaces is performed using a method according to any one of claims 1 to 7.

15. A method according to either of claims 13 or 14 comprising the applying of a reactive coating to both said surfaces by plasma deposition, introducing a coupling agent between said surfaces, and allowing said coupling agent to react with reactive groups on each surface.

16. A method according to claim 15 wherein the reactive groups are epoxide groups.

17. A method according to either of claims 15 or 16 wherein said coupling agent is a diamine.

18. A method according to either of claims 13 or 14 wherein said other surface includes nucleophilic groups able to react with said reactive groups so as to bring about adhesion.

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19. A method according to claim 18 wherein said nucleophilic groups are selected from amino or carboxylic acid groups.

20. A method for applying a reactive epoxy containing coating to a substrate substantially as hereinbefore described with reference to example 1.

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(71) Applicant *(for all designated States except US)*: **THE SECRETARY OF STATE FOR DEFENCE** [GB/GB]; Defence Evaluation and Research Agency, Ively Road, Farnborough, Hampshire GU14 0LX (GB).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: **WILLIS, Colin, Robert** [GB/GB]; CBD, Porton Down, Salisbury, Wiltshire SP4 0JQ (GB). **BADYAL, Jas, Pal, Singh** [GB/GB]; University of Durham, Science Laboratory, Dept. of Chemistry, South Road, Durham DH1 3LE (GB). **BREWER, Stuart, Anson** [GB/GB]; CBD, Porton Down, Salisbury, Wiltshire SP4 0JQ (GB).

(74) Agent: **BOWDERY, A., O.**; D/IPR, Formalities Section, Poplar 2, MOD Abbey Wood #19, Bristol BS34 8JH (GB).

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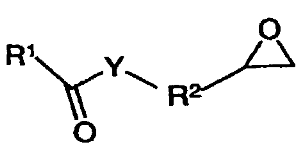
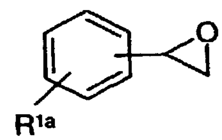
(54) Title: FUNCTIONALISED SOLID SURFACES



(I)



(IA)

(57) **Abstract:** A method for applying a reactive epoxy containing coating to a substrate, said method comprising subjecting said substrate to a plasma discharge in the presence of a compound of formula (I) or (IA) where R^1 or R^{1a} is an optionally substituted hydrocarbyl group or heterocyclic group; R^2 is an optionally substituted straight or branched alkylene chain; and Y is oxygen or a bond. Surfaces obtained in this way may subsequently be derivatised as desired, or adhered to other surfaces.

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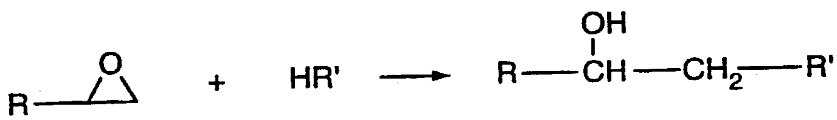
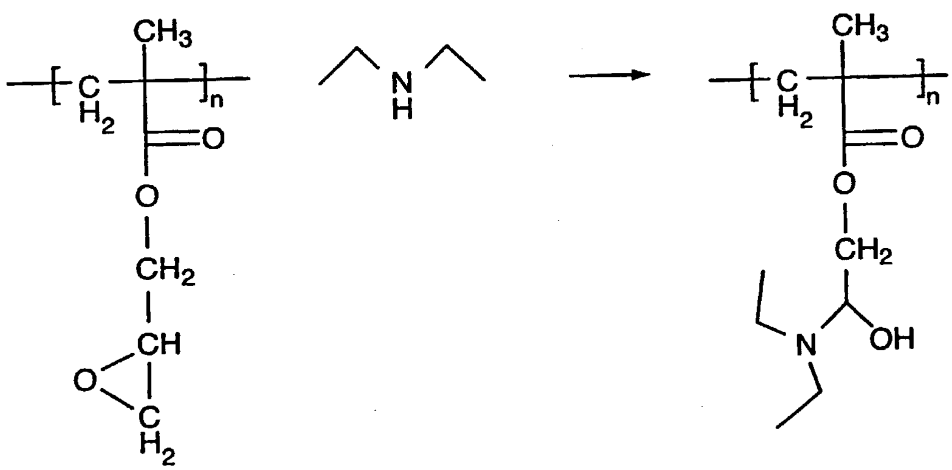
Scheme 1.



Scheme 3.



Scheme 2.

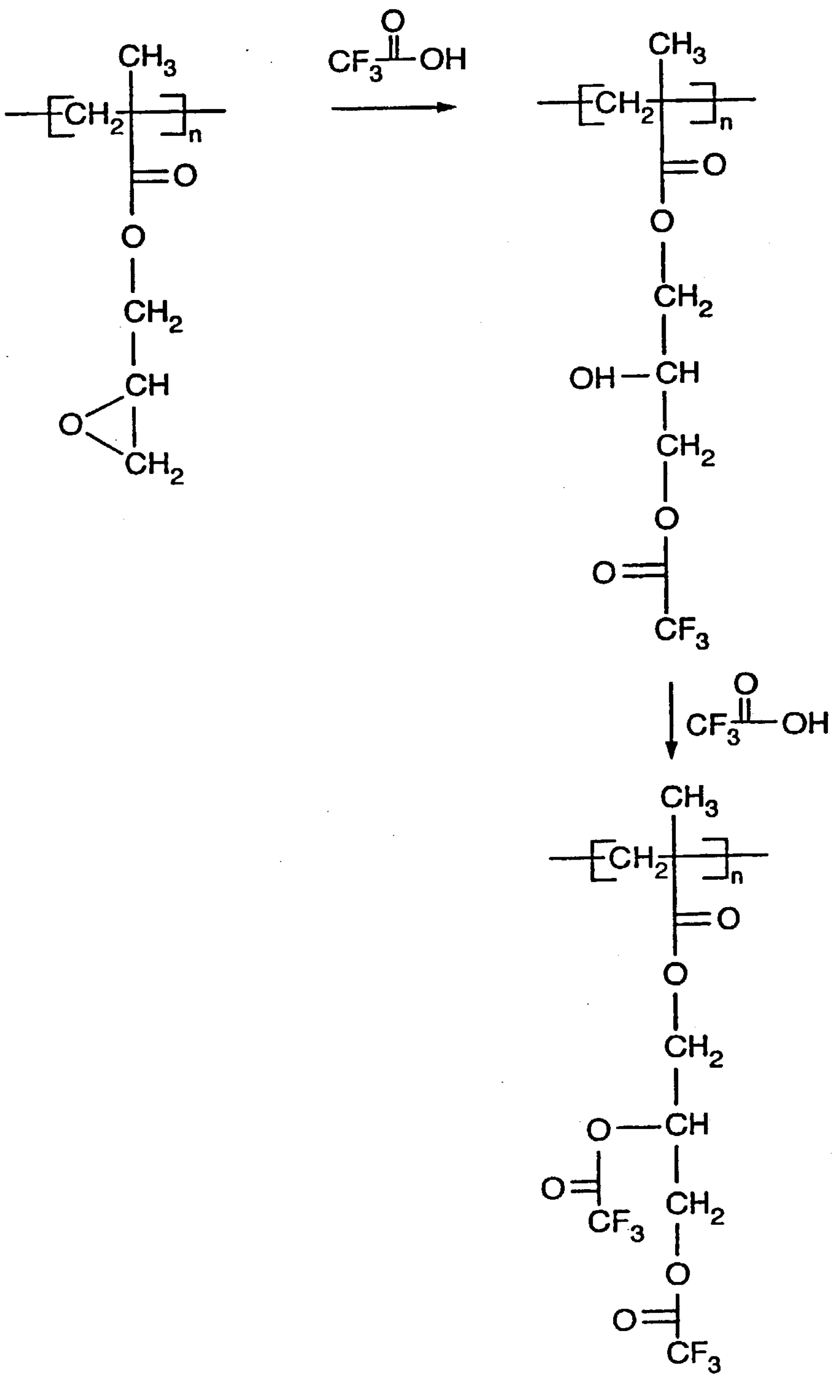


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Fig.1.

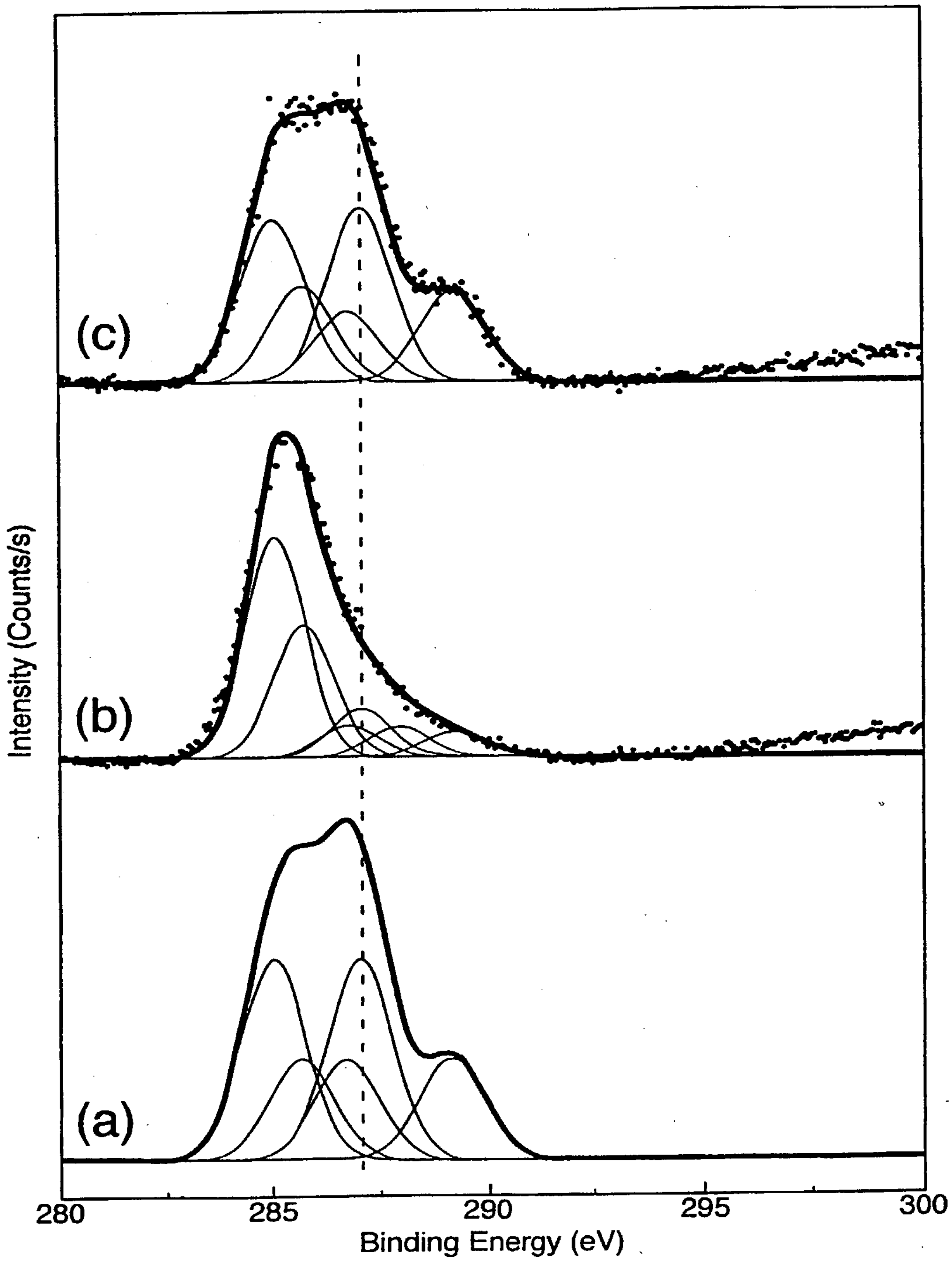

Fig.2.

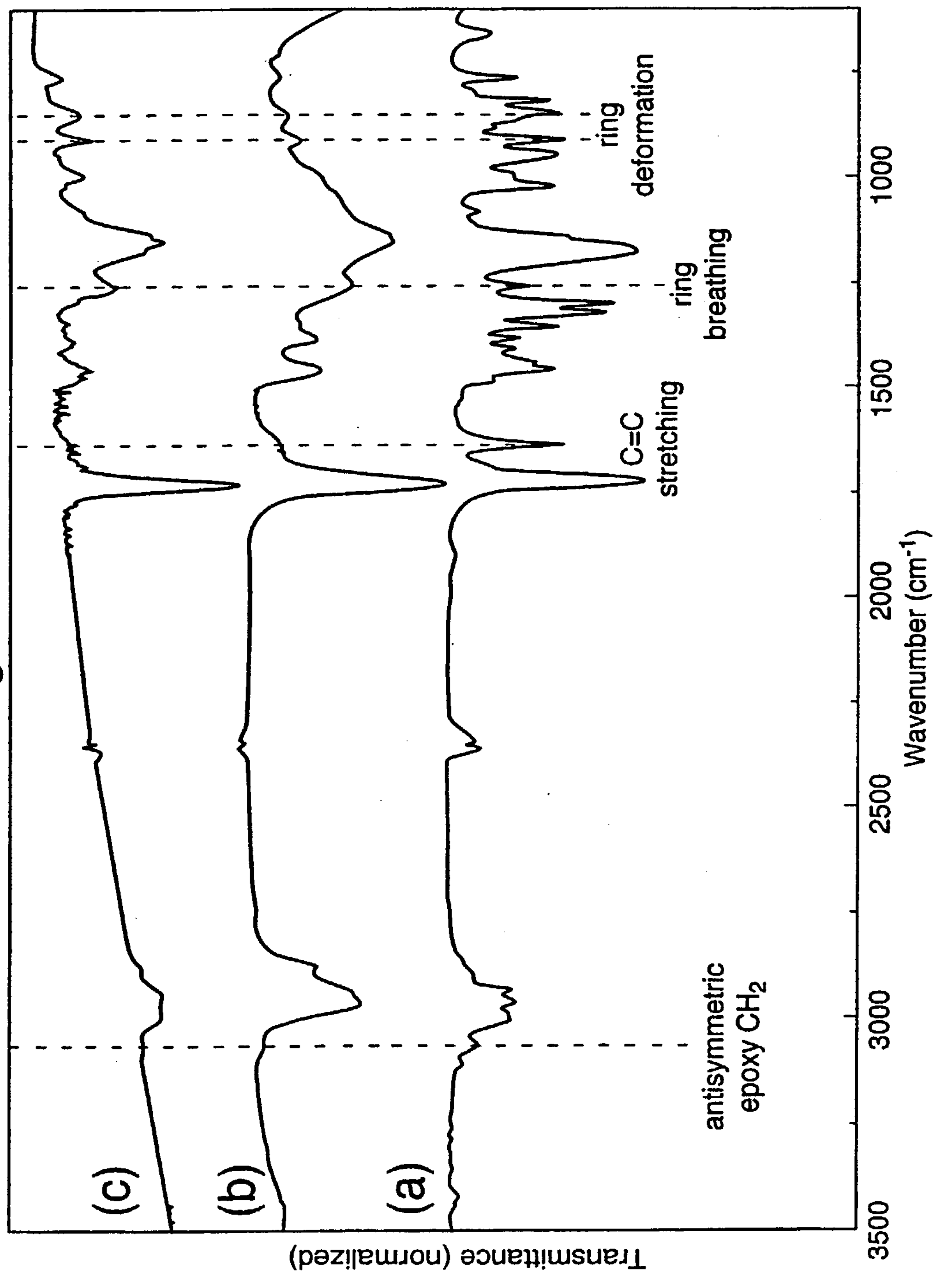
Transmittance (normalized)
(c)
(b)
(a)
antisymmetric epoxy CH_2
C=C stretching
ring breathing
ring deformation
3500
3000
2500
2000
1500
1000
Wavenumber (cm^{-1})

Fig.3.

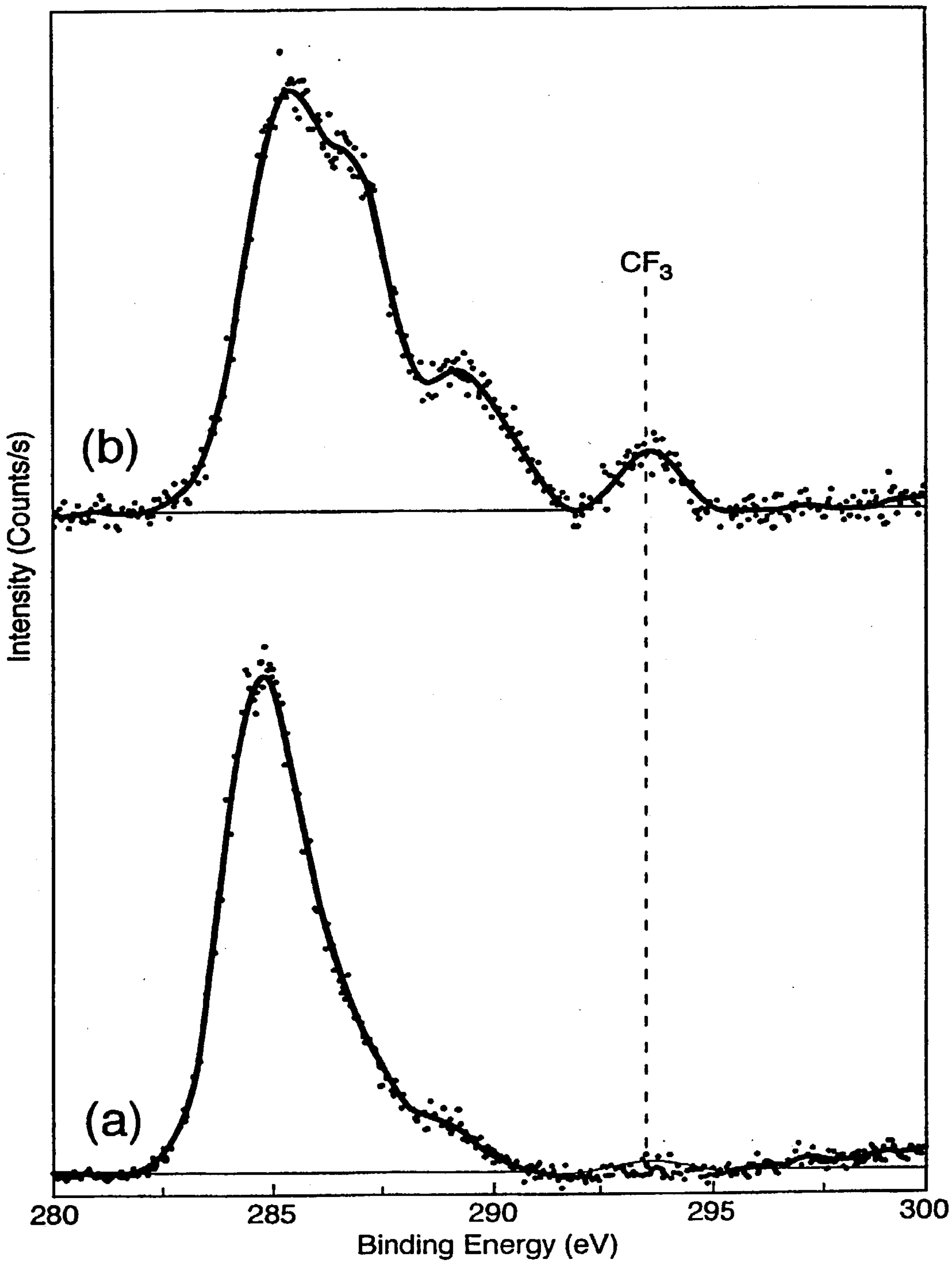

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Fig.4.

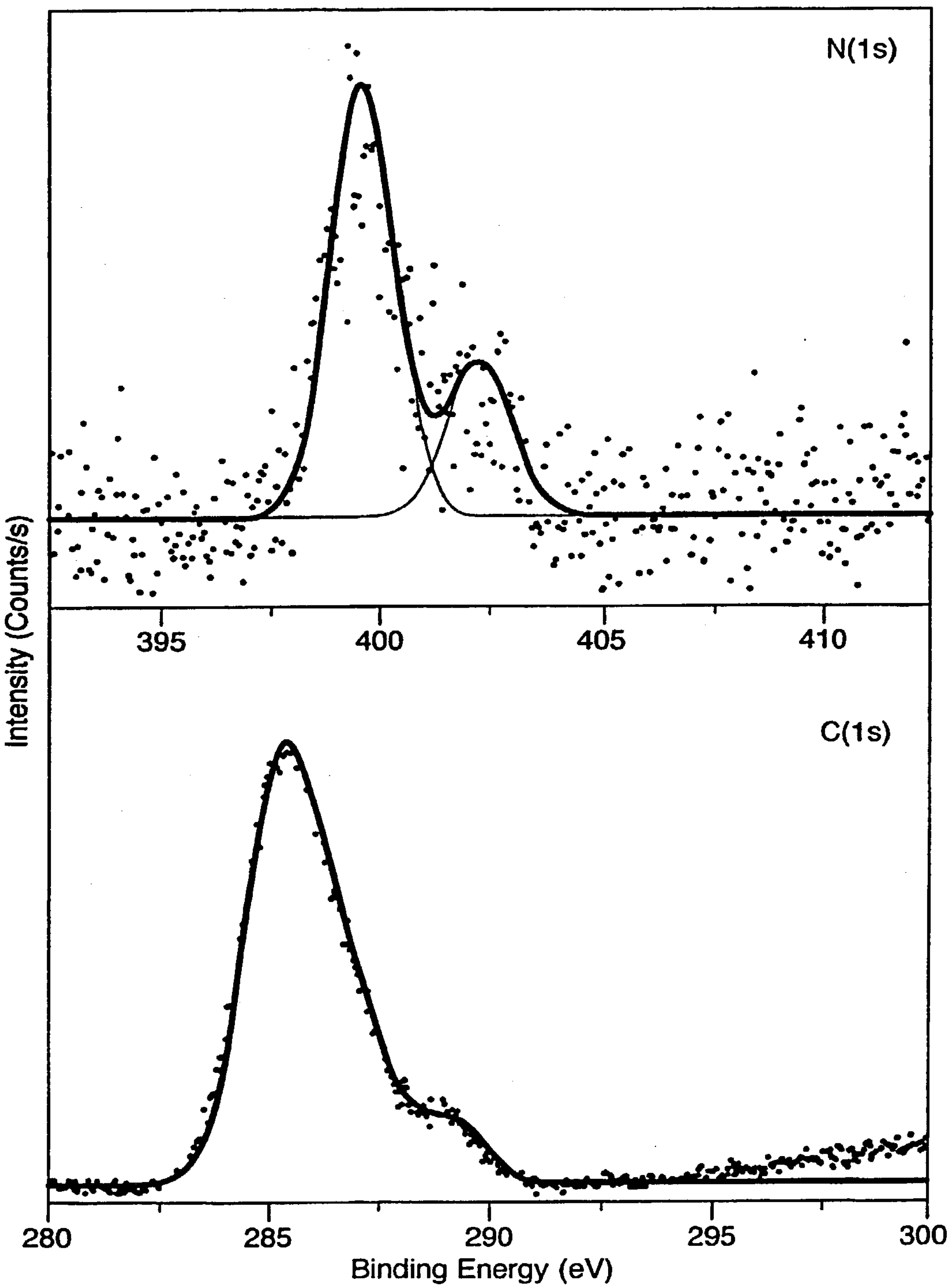
N(1s)
C(1s)
Intensity (Counts/s)
395
400
405
410
280
285
290
295
300
Binding Energy (eV)

Fig.5.

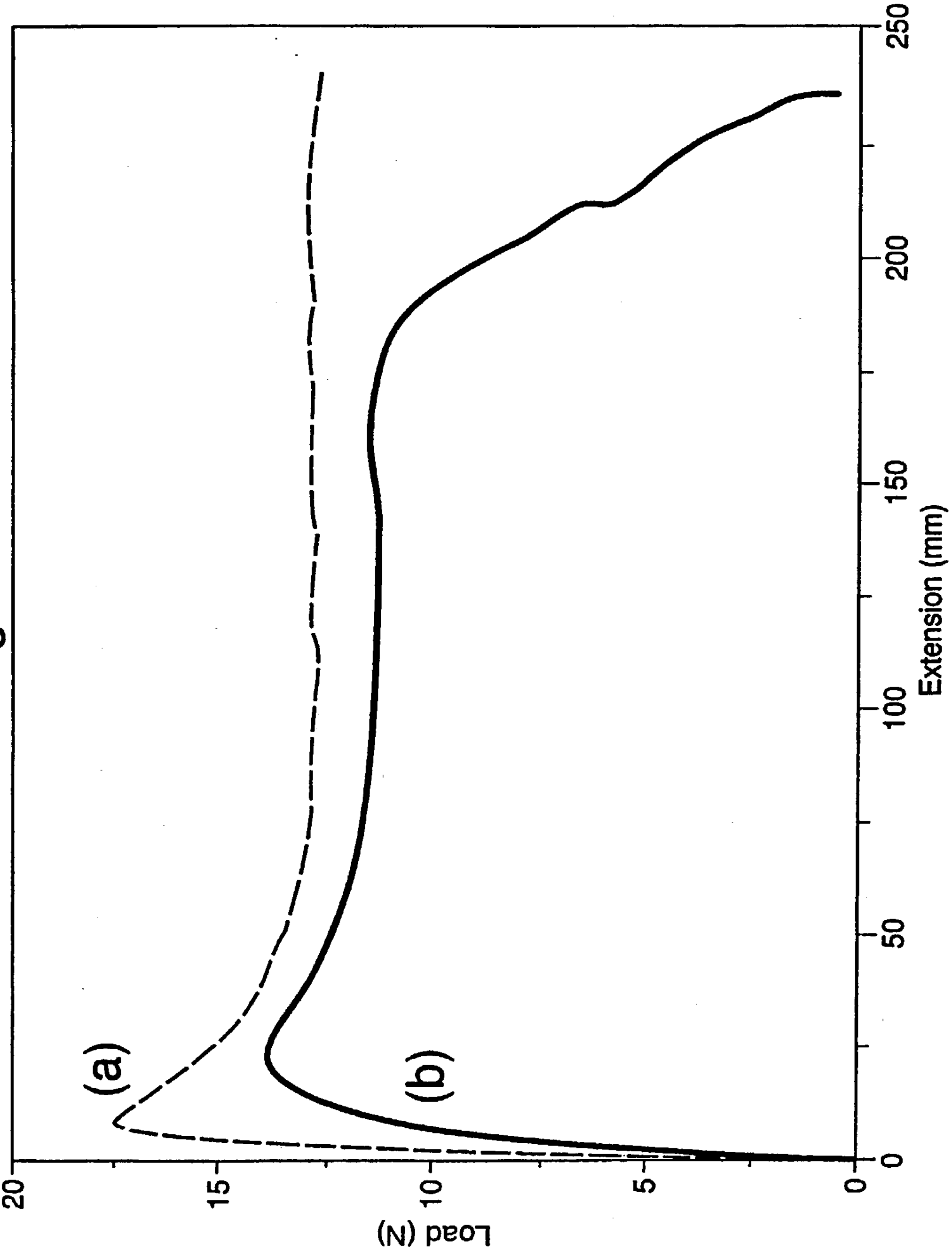

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Fig.6.

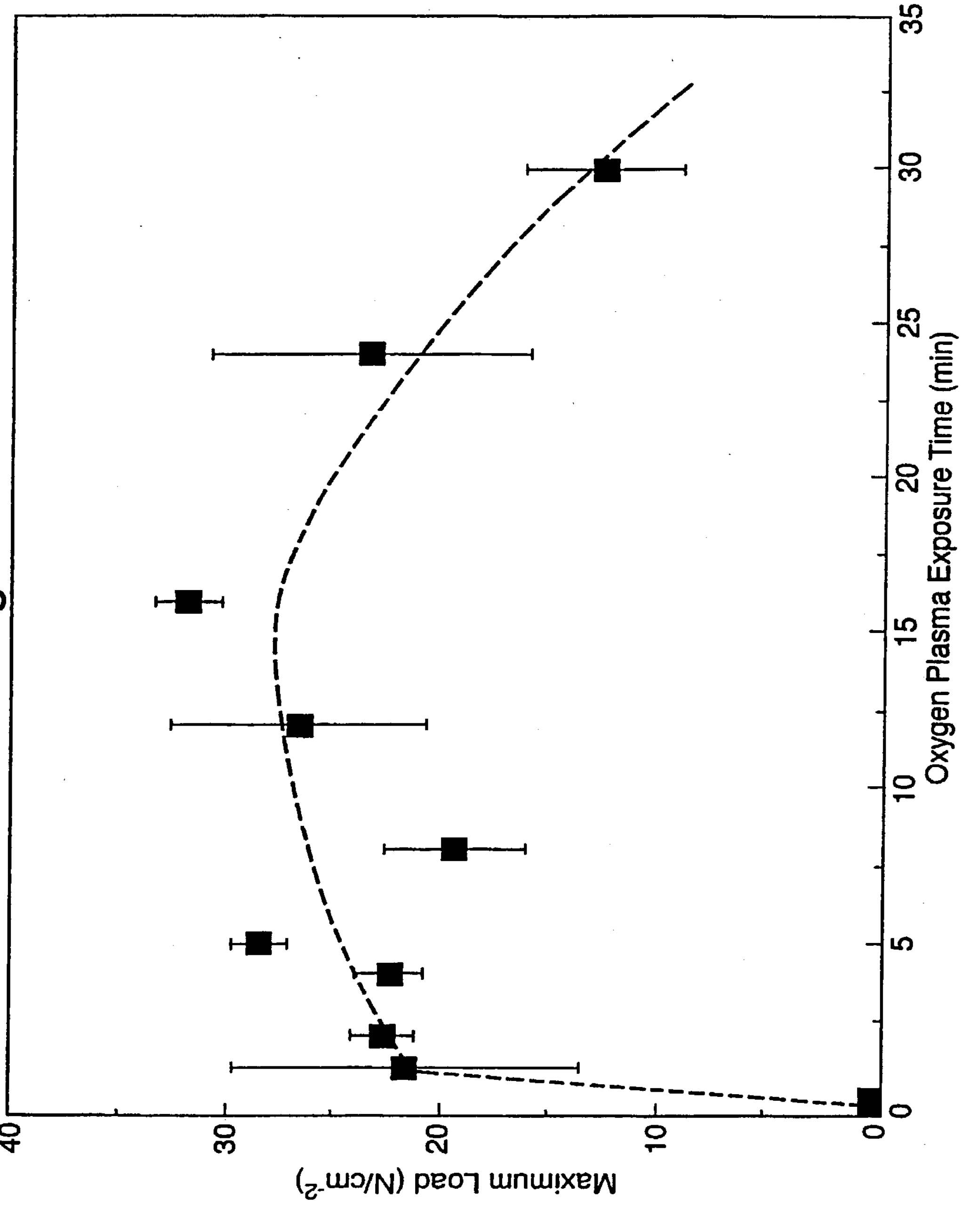

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Fig.7.

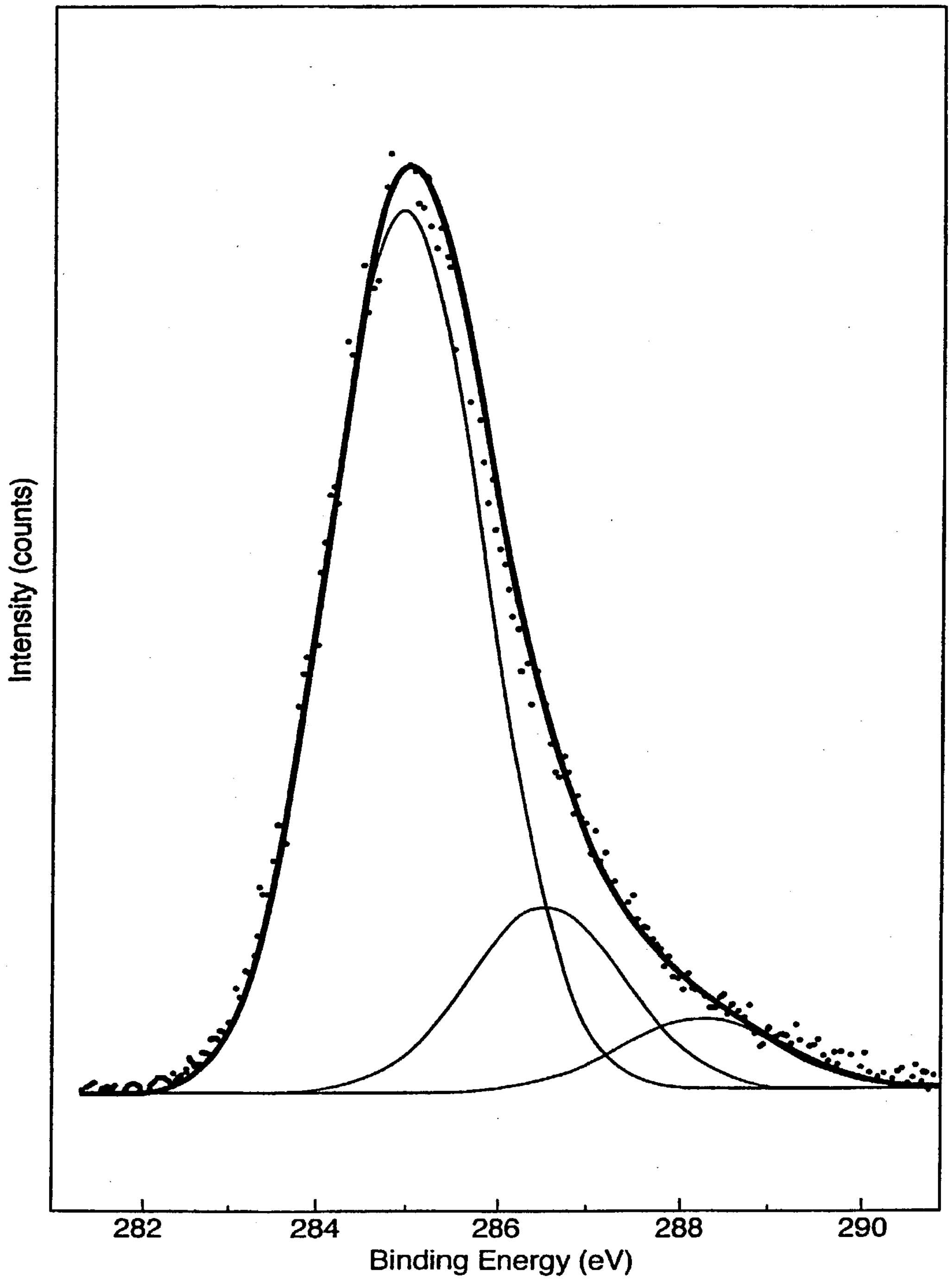
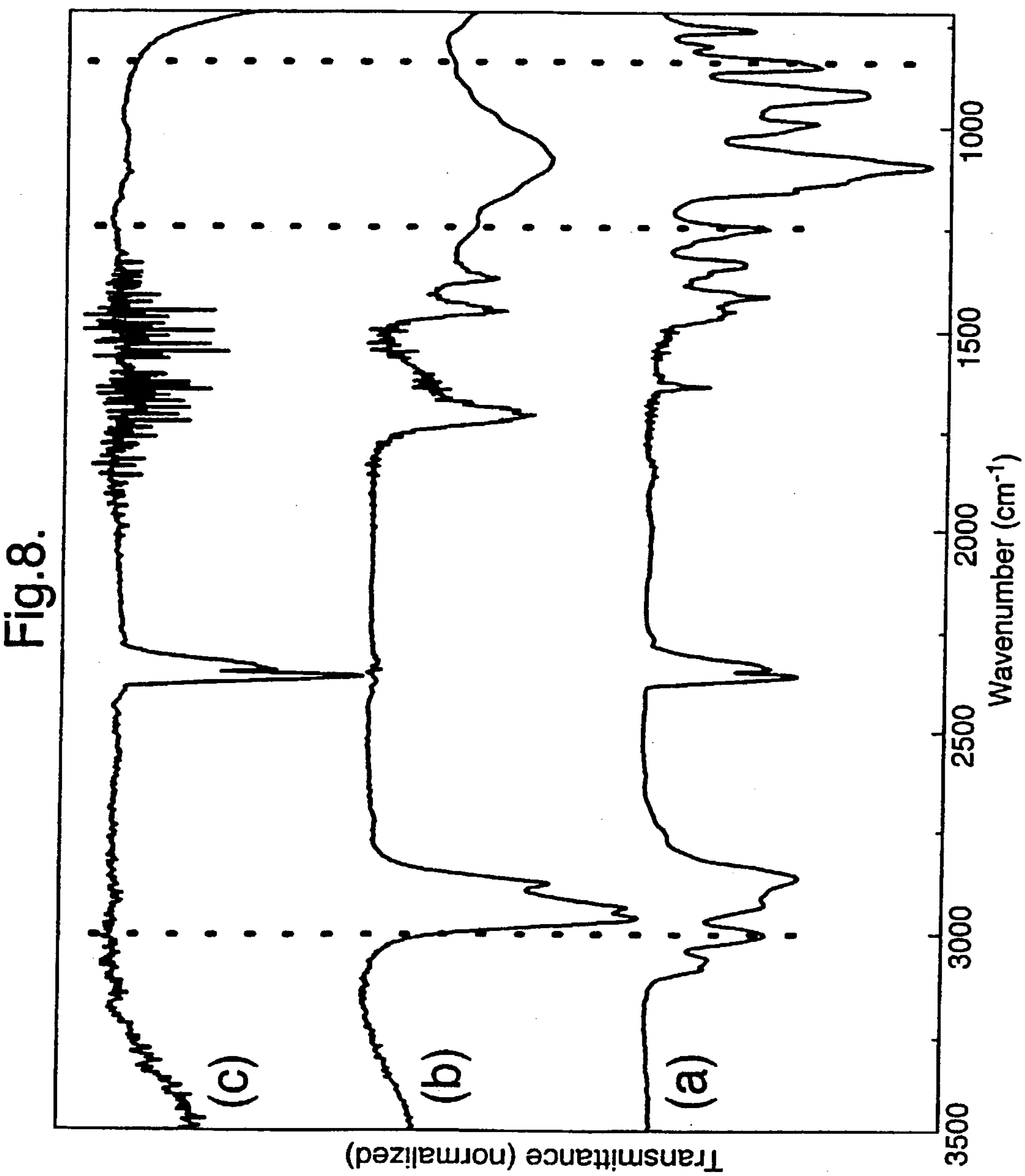
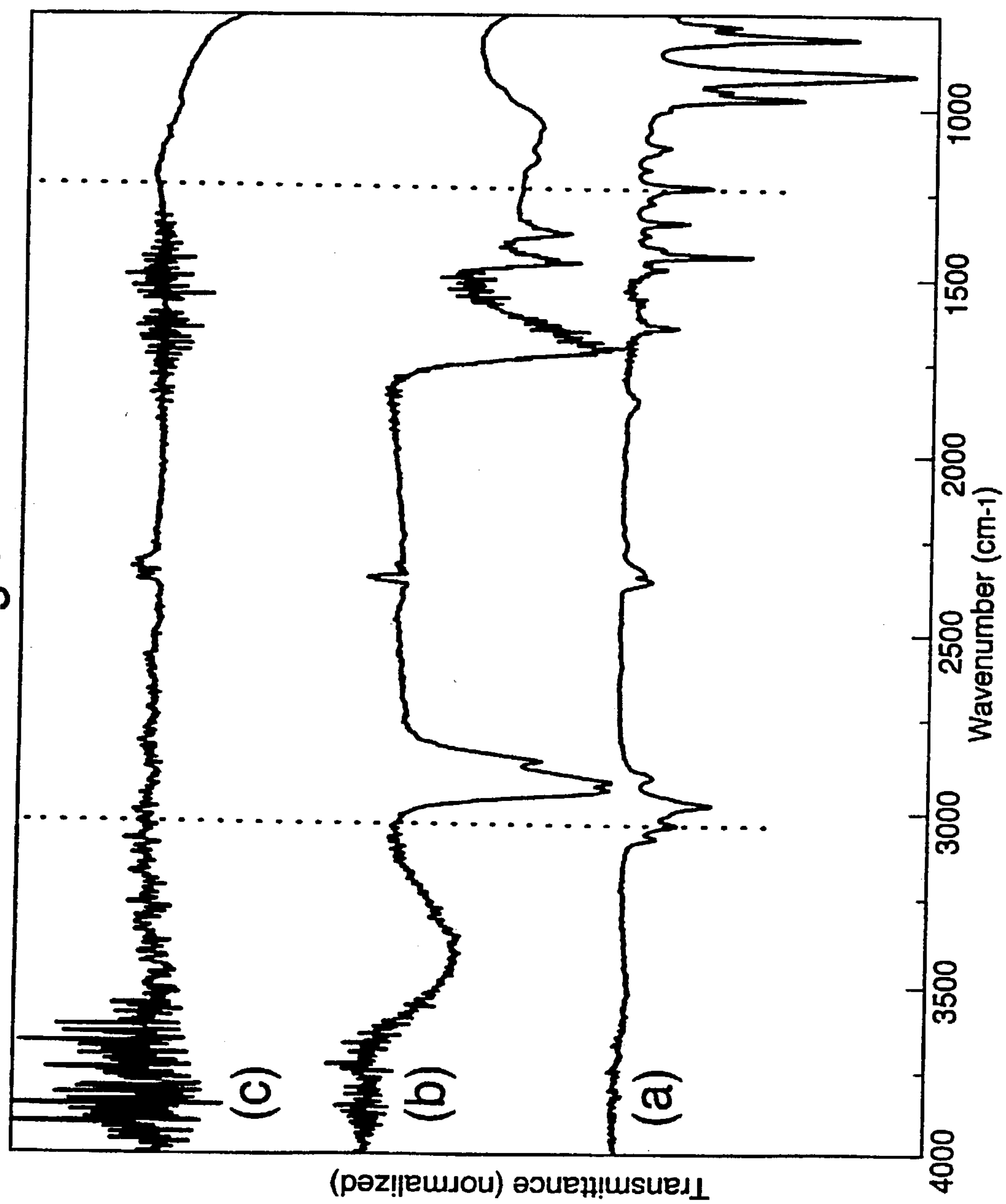


Fig.8.



Transmittance (normalized)
Wavenumber (cm^{-1})
3500
3000
2500
2000
1500
1000
(a)
(b)
(c)

Fig.9.


Transmittance (normalized)
(c)
(b)
(a)
4000
3500
3000
2500
2000
1500
1000
Wavenumber (cm-1)

Attorney Docket No.

DECLARATION FOR PATENT APPLICATION

☒ Original ☐ Supplemental ☐ Substitute ☐ PCT

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below), or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

FUNCTIONALISED SOLID SURFACES

the specification of which (check one)

☐ is attached hereto

☐ was filed on ____________ as U. S. Application Serial Number ____________

☒ was filed as PCT International Application Number PCT/GB00/02371 on 19 June 2000

and was amended under PCT Article 19 on

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the patentability of this application in accordance with Title 37, Code of Federal Regulations, § 1.56(a).

I hereby claim foreign priority benefits under Title 35, United States Code, § 119 (a) - (d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT international application which designated at least one country other than the United States of America, listed below and have also identified, by checking the box below, any foreign application for patent or inventor's certificate, or of any PCT international application having a filing date before that of the application on which priority is claimed.

Prior Foreign Applications			Priority Claimed		Copy Attached	
Application Number	Country	Foreign Filing Date	YES	NO	YES	NO
9914185.5	GB	18 June 1999	Yes			No
0001514.9	GB	25 January 2000	Yes			No

I hereby claim the benefit under Title 35, United States Code § 119(e) of any United States provisional application(s) listed below and claim the benefit under Title 35, United States Code, § 120 of any United States application(s), or § 365(c) of any PCT international application(s) designating the United States of America, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application(s) in the manner provided by the first paragraph of Title 35, United States Code, § 112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application:

10018727 .080902

U.S. Serial No.
For: "　　　"
Inventors:
Filed:
Declaration for Patent Application
Page 2

Parent Application Number	Filing Date	Status (Mark Appropriate Column Below)		
		Patented	Pending	Abandoned
PCT/GB00/02371	19 June 2000		Pending	

As a named inventor, I hereby revoke all prior powers and appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith:

KILPATRICK STOCKTON LLP, Suite 2800, 1100 Peachtree Street, Atlanta, Georgia 30309-4530

Attorney and/or Agent	Registration No.
Charles Y. Lackey	**22,707**
John M. Harrington	**25,592**
John S. Pratt	**29,476**
A. Jose Cortina	**29,733**
James L. Ewing, IV	**30,630**
Charles W. Calkins	**31,814**
George T. Marcou	**33,014**
40 **Bernard J. Graves, Jr.**	**33,239**
Dean W. Russell	**33,452**
Richard T. Peterson	**35,320**
Charles T. Simmons	**35,359**
Nora M. Tocups	**35,717**
Bruce D. Gray	**35,799**
Theodore R. Harper	**35,890**
Geoff L. Sutcliffe	**36,348**
Stephen B. Parker	**36,631**
Pat Winston Kennedy	**36,970**
Mitchell G. Stockwell	**39,389**
Michael J. Turton	**40,852**
Yoncha L. Kundupoglu	**41,130**

Attorney and/or Agent	Registration No.
Benjamin D. Driscoll	**41,571**
Alana G. Kriegsman	**41,747**
J. Steven Gardner	**41,772**
James J. Bindseil	**42,326**
Camilla Camp Williams	**43,992**
Carl B. Massey	**44,224**
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Kyle M. Globerman	**P46,730**
Tywanda L. Harris	**P46,758**
Kristin D. Mallatt	**P46,895**
Cynthia B. Rothschild	**P47,040**

I acknowledge the above-listed attorneys and agents and their firm Kilpatrick Stockton LLP represent my employer (if I am an employee and this application has been or will be assigned to my employer) or the entity with which I have contracted (if I am an

1017149

independent contractor and this application has been or will be assigned to such entity) and in such cases do not represent me individually. I further acknowledge I have not established, nor will I seek to establish, any personal attorney/client relationship with Kilpatrick Stockton LLP in connection with this application and understand that, should I require legal representation, I will obtain such, at my expense, other than through Kilpatrick Stockton LLP.

Send Correspondence to: John S. Pratt, Esq.
Kilpatrick Stockton LLP
1100 Peachtree Street, Suite 2800
Atlanta, Georgia 30309-4530

Direct telephone calls to: Dean W. Russell, Esq. (404) 815-6528

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

1-00 Full name of first inventor Colin Robert WILLIS
Inventor's signature Date 2/10/01
Residence GB
Citizenship GB
Post Office Address DSTL, Porton Down, Salisbury, Wiltshire. SP4 0JQ. GBX

2-00 Full name of second inventor Stuart Anson BREWER
Inventor's signature Date 15/10/01
Residence GB
Citizenship GB
Post Office Address DSTL, Porton Down, Salisbury, Wiltshire. SP4 0JQ. GBX

Full name of second inventor Jas Pal Singh BADYAL
Inventor's signature Date
Residence GB
Citizenship GB
Post Office Address . University of Durham, Science Laboratory, Dept. of Chemistry, South Road, Durham. DH1 3LE.

10018727 .080902

Attorney Docket No.

DECLARATION FOR PATENT APPLICATION

☒ Original ☐ Supplemental ☐ Substitute ☐ PCT

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below), or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

FUNCTIONALISED SOLID SURFACES

the specification of which (check one)

☐ is attached hereto

☐ was filed on __________ as U. S. Application Serial Number __________

☒ was filed as PCT International Application Number PCT/GB00/02371 on 19 June 2000

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Atlanta, Georgia 30309-4530

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Full name of first inventor Colin Robert WILLIS
Inventor's signature Date
Residence GB
Citizenship GB
Post Office Address DSTL, Porton Down, Salisbury, Wiltshire. SP4 0JQ.

Full name of second inventor Stuart Anson BREWER
Inventor's signature Date
Residence GB
Citizenship GB
Post Office Address DSTL, Porton Down, Salisbury, Wiltshire. SP4 0JQ.

3-00 Full name of second inventor Jas Pal Singh BADYAL
Inventor's signature Jas Pal Badyal Date 16th April 2002
Residence GB
Citizenship GB
Post Office Address University of Durham, Science Laboratory, Dept. of Chemistry, South Road, Durham, DH1 3LE. GBX